

PHOSPHATE AS AN ELECTRON ACCEPTOR AND PHOSPHINE AS A BIOSIGNATURE. M. A. Pasek¹,

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Introduction: Phosphate is not typically viewed as an electron acceptor due to its large endergonic reduction potential. However, the gas phosphine, PH₃, is known to be a trace but ubiquitous atmospheric gas [1] and it is a plausible product of a potential biologically-driven phosphate reduction process. The ultimate source of this phosphine is unclear and has troubled phosphorus (P) biogeochemists.

Recently we proposed the reduced oxidation state P compounds phosphite (H₂PO₃⁻) and hypophosphite (H₂PO₂⁻) as sources of the reducing power leading to phosphine [2]. This reaction, driven by the disproportionation reaction:



can generate phosphine at concentrations that have been seen in atmospheric measurements if the percentage of P that is reduced is about 5 to 20% of the total dissolved phosphorus.

Florida water samples have shown that both phosphite and hypophosphite are present at these concentrations [2], suggesting that these compounds may be the ultimate source of phosphine. Alternatively, phosphine may be generated by the corrosion of phosphides in anthropogenic samples [3]. The ultimate source of phosphine, and the rationale for reducing P (presumably by microbes) remains unclear.

In either case, the presence of reduced oxidation state P in an oxidizing environment like the earth's surface would imply active biological cycling of this element, and may be useful for identifying biosignatures on other worlds.

Hypotheses: The origin of phosphine in the atmosphere and reduced P compounds in water are unclear, but may be produced by microbes, or alternatively, these may be a product of modern industry.

Natural P reduction from microbes. Reduction of phosphate is endergonic. One possible route for synthesis of reduced P compounds is as a byproduct of phosphonate metabolism. Phosphonates, with C-P bonds, have recently been demonstrated to be important parts of both P and C biogeochemical cycles [4]. Phosphite generation from phosphonates is spontaneous, and this ion may be an important part of the P biogeochemical cycle [4].

The disproportionation reaction (1) has not been demonstrated yet, and, if this reaction is active, then it is unclear if the reaction is biologically or abiotically mediated.

Anthropogenic phosphine. Phosphine is generated by the reaction of phosphides with acid, including iron phosphides, found as contaminants of industrial iron and steel.

Implications of P electron transfer to Astrobiology: If atmospheric phosphine owes its origin to anthropogenic sources, then the detection of PH₃ in an oxygenated atmosphere could point to an inhabited planet with an active civilization. However, if the majority of the earth's phosphine is generated by microbial reduction of phosphate to phosphite or hypophosphite, then the presence of PH₃ in an oxygenated atmosphere might be a biosignature only.

If the latter, several questions are posed by the microbial reduction of phosphate: 1) Why? What is the environmental and evolutionary rationale for phosphate reduction? 2) How? What biochemical pathways are driving phosphate reduction? And 3) Who? What microbes are responsible for this chemistry? If phosphine is production by microbes, then are there specific species of microbes that do this?

Phosphate reduction is an unusual process. However, constraining the specifics of this reaction may in turn give us better understanding of the role of biology in choosing its electron acceptors, and the possibility that this process is ubiquitous in life.

References: [1] Glindemann D. et al. (2005) *Ecol Eng*, 24, 457-463. [2] Pasek M. A. et al. (2014) *PNAS*, 111, 15468-15473. [3] Roels J. and Verstraete W. (2004) *Sci Total Env*, 327, 185-196. [4] Karl D. M. (2014) *Ann Rev Marine Sci*, 6, 279-337.